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C-NO₂ Dissociation Energies and Surface Electrostatic Potential Maxima in
Relation to the Impact Sensitivities of Some Nitroheterocyclic Molecules

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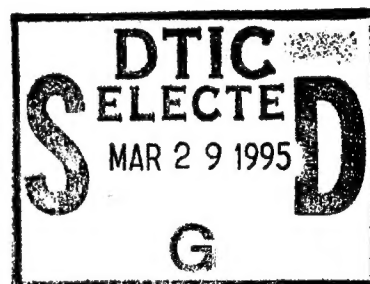
Peter Politzer and Jane S. Murray

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Department of Chemistry
University of New Orleans
New Orleans, LA 70148



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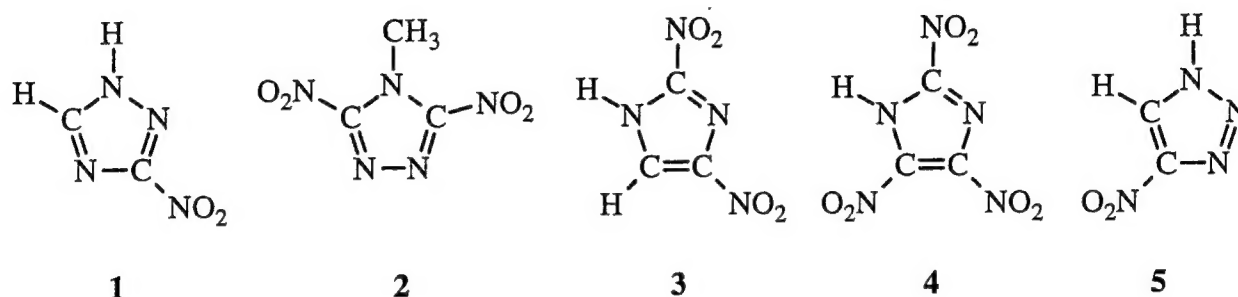
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13. ABSTRACT (Maximum 200 words) A nonlocal density functional procedure (GAUSSIAN 92/DFT, BLYP, 6-31G**) has been used to compute the dissociation energies of the C-NO ₂ bonds in five unsaturated nitroheterocyclic molecules. These show a definite correlation with the maxima of the surface electrostatic potentials above these bonds, which may explain why these potential maxima are one of the properties that appear in an earlier analytical representation of the measured impact sensitivities of nitroheterocyclic compounds.															
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Introduction

The strength and other properties of C–NO₂ bonds are of considerable importance in the area of energetic materials, since the rupture of this linkage is believed to be a key factor in many decomposition processes [1-10]. We have accordingly computed the dissociation energies of the C–NO₂ bond in the heterocyclic molecules **1** - **5**, in order to examine directly their relationship, if any, to the measured impact sensitivities of these compounds. We also relate our results to the electrostatic potentials associated with these bonds, which have been involved in earlier sensitivity correlations [9-11].



Methods

Optimized geometries, energies and vibration frequencies were calculated for **1** - **5** and their homolytic dissociation products with the density functional option of GAUSSIAN 92/DFT [12]. The Becke exchange and the Lee, Yang and Parr correlation functionals were used [13,14], with a 6-31G** basis set. Zero-point energies were also calculated. This computational approach has been shown to be very competitive with other correlated procedures [15].

The electrostatic potential $V(\mathbf{r})$ that the nuclei and electrons of a molecule create in the surrounding space is given rigorously by eq. (1):

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}') d\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \quad (1)$$

Z_A is the charge on nucleus A, located at \mathbf{R}_A , and $\rho(\mathbf{r})$ is the electronic density. $V(\mathbf{r})$ is a real physical property, and can be determined experimentally by diffraction techniques as well as computationally [16]. We have recently computed the *ab initio* HF/6-31G* electrostatic potentials of a group of nitroheterocyclic molecules (including **1** - **4**), using HF/3-21G* geometries [11]. For present purposes we extended these calculations to include **5**, and we will focus specifically upon the maximum value of $V(\mathbf{r})$ on the molecular surface above each of these bonds, $V_{S,\max}(\text{C} - \text{NO}_2)$. In accordance with the suggestion of Bader *et al* [17], the surface is taken to be the 0.001 au contour of the electronic density $\rho(\mathbf{r})$.

Results

Table 1 lists the measured impact sensitivities of **1** - **5**, the C-NO₂ dissociation energies (including zero-point corrections), and the maxima of the surface potentials above the C-NO₂ bonds. The sensitivities are taken from the compilation of Storm *et al* [18]; the shorter is the impact drop height, h_{50} , the greater is the sensitivity.

The magnitudes of the C-NO₂ dissociation energies are reasonable, being in the same range as those observed experimentally for other systems [5,19]. In any case, our focus shall be upon their relative values.

Discussion

If the impact sensitivities of these compounds depended only upon the ease of C-NO₂ bond-breaking, then sensitivity would be expected to increase as the C-NO₂ dissociation energy decreases. The data in Table 1 show that there is no general correlation of this sort, but suggest that one may exist on a more limited scale. For example, **1** and **2** have the same ring structure, as do **3** and **4**. Within each of these pairs, the introduction of an additional nitro group has the twin effects of decreasing C-NO₂ bond strength and increasing impact sensitivity. It may be, therefore, that there does exist a close relationship between these two factors within certain classes of compounds.

On the other hand, we believe that certain molecules have their own very specific decomposition mechanisms, in which C-NO₂ bond rupture may play a relatively minor role. Some hydroxynitroaromatics may fit this category [20], as well as some picryl triazoles [21]. We consider **5** to be another example of such a compound. It is very sensitive to impact, more so than any of the others in Table 1, yet has the highest C-NO₂ dissociation energy of this group. By means of a detailed density functional computational study (GAUSSIAN 92/DFT, BP86, 6-31G**) [22], we have shown that **5** can decompose through ring opening followed by N₂ evolution, the overall process being exothermic. The C-NO₂ bond remains intact during these steps.

We have recently shown that the electrostatic potentials computed on the surfaces of nitroheterocycles have maxima above the C-NO₂ bonds [11]. We were able to develop an accurate analytical representation, given below as eq. (2), of the impact sensitivities of a group of these compounds, including **1** - **4**. It is in terms of these potential maxima plus a computed property Π that is a measure of the internal charge separation in a molecule [23], the local polarity that is present even when the overall dipole moment is zero. (In eq. (2), it is only the most positive $V_{S,max}(C-NO_2)$ for each molecule that is used.)

$$h_{50} = \alpha [\Pi^2 V_{S,\max}(\text{C}-\text{NO}_2)]^{-1} + \beta \quad (2)$$

All of the $V_{S,\max}(\text{C}-\text{NO}_2)$ for each molecule are listed in Table 1. Within each of the pairs with the same ring structure, 1, 2 and 3, 4, the introduction of an additional $-\text{NO}_2$ makes the other $V_{S,\max}(\text{C}-\text{NO}_2)$ more positive. This presumably reflects decreases in electronic charge in the other $\text{C}-\text{NO}_2$ regions due to the electron-withdrawing power of the added nitro group, and suggests a weakening of those $\text{C}-\text{NO}_2$ bonds, as is indeed observed (Table 1).

There is in fact a definite correlation between the computed $\text{C}-\text{NO}_2$ dissociation energies and the magnitudes of $V_{S,\max}(\text{C}-\text{NO}_2)$ for the molecules in Table 1. The more positive is $V_{S,\max}(\text{C}-\text{NO}_2)$, the weaker is that $\text{C}-\text{NO}_2$ bond. This is shown in Figure 1; the linear correlation coefficient is $R = 0.915$. (If the outlier corresponding to bond **a** of **3** is removed, the correlation improves to $R = 0.981$.) In this context it is relevant to note the work of March *et al* in using density functional theory to develop relationships between bond dissociation energies and electrostatic potentials [24,25].

In view of the correlation shown in Figure 1, it seems reasonable to speculate that the role of $V_{S,\max}(\text{C}-\text{NO}_2)$ in eq. (2) is to represent the strength of the weakest $\text{C}-\text{NO}_2$ bond in each molecule. As was pointed out above, this is evidently an important factor in determining impact sensitivity, but it is not sufficient to explain the variation in this property among different classes of nitroheterocycles. Eq. (2) indicates that the extent of charge separation within the molecule also needs to be taken into account.

Summary

The results that have been presented demonstrate anew the significance of the positive electrostatic potentials associated with $\text{C}-\text{NO}_2$ bonds. Some time ago, we already showed that there are buildups of positive potential above these bonds in nitroaromatics and unsaturated nitroheterocycles [26-30], which can serve as initial sites for nucleophilic attack. We found subsequently that the potentials at the midpoints of nitroaromatic $\text{C}-\text{NO}_2$ bonds, estimated crudely from the carbon and nitrogen atomic charges, correlate roughly with the compounds' impact sensitivities [9,10]. Most recently, more accurate and physically meaningful representations of impact sensitivities were developed in terms of surface potential maxima and the degrees of internal charge separation, for both nitroaromatics and nitroheterocycles [11]. For the latter, the potential maxima above the $\text{C}-\text{NO}_2$ bonds have now been linked to their dissociation energies, as one of the important factors typically (but not invariably) determining impact sensitivity.

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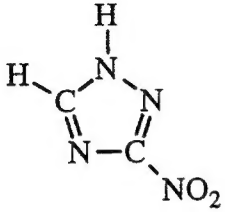
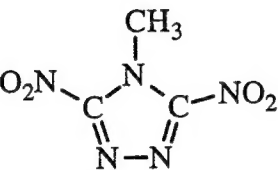
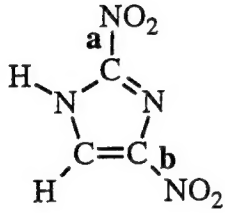
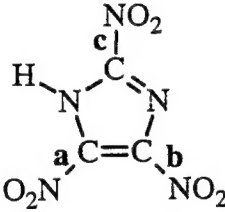
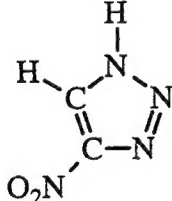
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Figure Caption

Figure 1. Plot of $V_{s,max}(C-NO_2)$ vs. $C-NO_2$ dissociation energy for the molecules in Table 1. The linear correlation coefficient is 0.915.

Table 1. Measured impact sensitivities^a and computed properties.

	Molecule	Impact sensitivity, h_{50} , cm. ^a	C-NO ₂ dissociation energy, kcal/mole ^b	$V_{S,max}(C-NO_2)$ kcal/mole
1		>320	63.0	21.9
2		155	57.1	47.5
3		105	a: 63.2 b: 63.9	a: 40.0 b: 25.8
4		68	a: 56.6 b: 59.6 c: 54.8	a: 49.6 b: 40.4 c: 52.4
5		25	65.6	20.5

^aReference 18. The smaller is the value of h_{50} , the greater is the sensitivity.^bThe difference in zero-point energies is included.

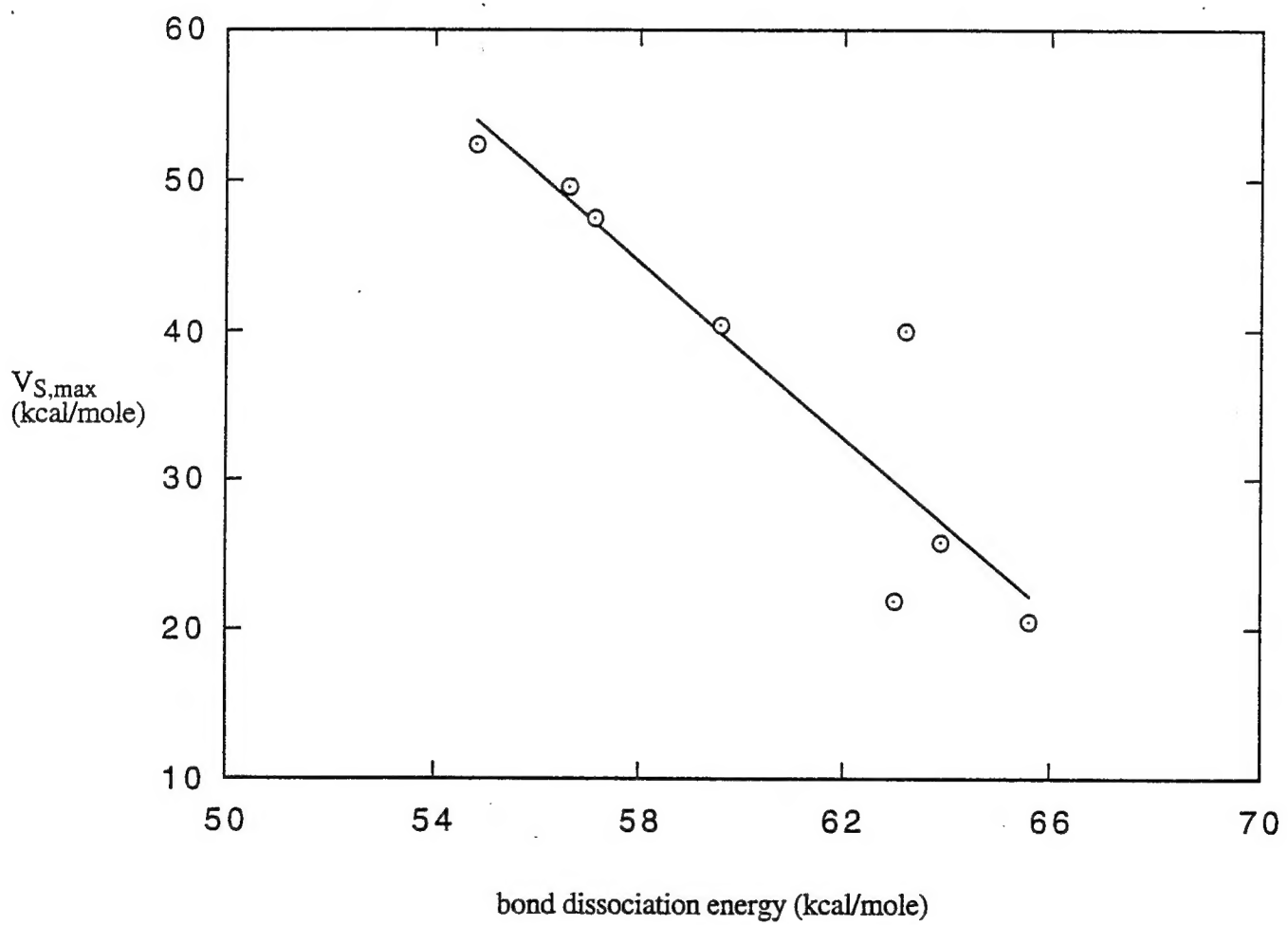


Figure 1.